

TITLE**POLYESTERS CONTAINING MICROFIBERS, AND  
METHODS FOR MAKING AND USING SAME**

5                   This application claims the benefit of U.S. Provisional  
Application No. 60/467,342, filed May 2, 2003.

**FIELD OF THE INVENTION**

10                  The present invention is directed to polyesters containing  
microfibers, and to methods for making and using the polyesters.

**BACKGROUND OF THE INVENTION**

15                  Thermoplastic polyester resins such as polyethylene  
terephthalate and polybutylene terephthalate have excellent  
mechanical properties, chemical resistance and dimensional stability  
and are widely used in applications such as injection molding, textile  
and monofilament fibers, and films.

20                  Fiber or particulate modification of thermoplastics, including  
thermoplastic polyesters, is well known and widely practiced. Fiber  
and particulate additives can be used as a filler to lower the overall  
costs of the thermoplastic. Additives can also be used to modify and  
improve mechanical properties or modify chemical resistance. Fibers  
can be added to polymers to make composites including advanced  
engineering composites, wherein the reinforcing fibers significantly  
25                  modify the properties of the thermoplastic material. Advanced  
composites containing fibers such as Kevlar® fibers or carbon fiber  
with a thermoplastic polyester matrix are known and widely used in  
articles such as sporting goods.

30                  Recently, much research is being conducted to learn how  
finely divided additives with particle sizes on the order of nanometers  
can be used to modify material properties. For example, US Patent No.  
6,020,419 discloses the effect of relatively small amounts of a modifier

can significantly impact properties such as scratch resistance or electrical properties.

5 A need remains for improved polymeric materials that can withstand melt processing while maintaining their structural properties, and also for polymeric materials having abrasion resistance when used in applications such as films.

### **SUMMARY OF THE INVENTION**

10 One aspect of the invention is a polyester composition comprising a polyester and microfibers. In some preferred embodiments, the polyester composition comprises from about 0.01 to about 15 weight percent of microfibers, based on the total weight of the polyester composition. In some embodiments, the polyester is a homopolymer. In some embodiments, the polyester is a copolymer. In some preferred embodiments, the polyester is polyethylene 15 terephthalate. In other preferred embodiments, the polyester is a copolyester comprising ethylene terephthalate and one or more comonomers. In some preferred embodiments, the microfibers are organic.

20 Another aspect of the invention is a process for making a polyester composition comprising a polyester and one or more microfibers. The process includes providing a slurry containing the microfibers, contacting the slurry with one or more polymerizable components. In some embodiments, the polymerizable components 25 comprise monomers.

Another aspect of the invention is a process for making a monofilament. The process includes melt spinning a polyester containing from about 0.01 to about 15 percent microfibers.

30 A further aspect of the invention is a molded part made from a polyester containing from about 0.01 to about 15 weight percent microfibers.

A further aspect of the invention is a cast film made from a polyester containing from about 0.01 to about 15 weight percent microfibers. In some embodiments, the film is uniaxially or biaxially oriented.

5 These and other aspects of the invention will be apparent to those skilled in the art in view of the following disclosure and the appended claims.

#### **DETAILED DESCRIPTION OF THE INVENTION**

10 The present invention provides polyesters and polyester compositions containing microfibers. The polyesters offer improved melt processing and improved polymer abrasion in comparison to conventional polyesters not containing microfibers. The present invention also includes processes for making the polyesters containing  
15 microfibers. The processes provide improved dispersion of the microfibers in the polyesters such that the particles within the polymer are well separated and do not reaggregate. While it is not intended that the present invention be bound by any particular theory, it is believed that some of the observed improved properties of polyesters containing microfibers and the dispersion of the microfibers within the polyesters, as disclosed herein, are due in part to an interaction  
20 between functional groups on the polyesters and functional groups on the microfibers. The term "polyester composition" is used herein to refer to compositions including a polyester, microfibers, and any optional additives and/or processing aids that can be present.  
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30 The term "microfibers", as used herein, refers to particulate materials that can be generally described as fibers because of their aspect ratios. Preferred microfibers for use in the polyesters and in the processes for making the polyesters as disclosed herein have aspect ratios from about 10:1 to about 500:1, more preferably from about 25:1 to about 300:1. For example, some preferred fibers have volume

average lengths of about 0.1 to about 100 microns and diameters of about 8 to 12 microns. Generally the microfibers also have an average surface area ranging from 25 to 500 square meters per gram. However, these dimensions are approximations only. Moreover, the 5 use of the term "diameter" is not intended to convey that the microfibers are required to be cylindrical in shape or circular in cross-section. The microfibers may also be referred to as "nanofibers", which is an indication that in at least one dimension, the size of the particulate materials is on the order of nanometers. Microfibers, 10 particularly when in the form of a slurry or dispersion, may also be referred to as "micropulp", or as "nanopulp". The term "microfibers" is used herein to refer to the fibers whether or not they are in the form of a slurry.

For incorporation into polyesters, the microfibers can be 15 provided in the form of a slurry. The slurry includes a liquid and the microfibers dispersed therein. The slurry preferably contains at least about 0.01 weight percent of microfibers, based on the total weight of the slurry and microfibers. Although the slurry can contain up to about 25 or 50 weight percent fibers, the practical upper limit of the amount of 20 microfibers that can be in the slurry is determined by handling and equipment requirements. Preferably, the slurry contains at least about 0.1 weight percent of microfibers. Also preferably, the slurry contains about 15 weight percent or less of microfibers, based on the total weight of the slurry and microfibers, more preferably about 10 weight 25 percent or less, and even more preferably, about 5 weight percent or less. In some preferred embodiments, the slurry contains from about 0.1 weight percent to about 2.5 weight percent microfibers, and even more preferably, the slurry contains from about 0.2 to about 1 weight percent microfibers. The slurry can be incorporated into the polyester 30 using conventional mixing and pumping equipment.

A slurry of the microfibers can be made from a variety of starting materials such as, for example, pulp, short fiber, fibrils or mixtures derived therefrom. The starting materials are generally in fiber form and may also be referred to herein as "fibers". The starting materials are processed into microfibers. Processing can be accomplished by contacting the starting material with a liquid medium and agitating the starting material and liquid medium to reduce the size of and modify the starting material. The processing of the fibers to form the microfibers preferably results in the microfibers being substantially uniformly dispersed in the liquid medium. Optionally, the liquid medium can contain one or more solid components. The presence of such solid components may aid in the processing. Processes for preparing a slurry of microfibers suitable for use in making the polyesters are described in concurrently-filed and co-owned patent application entitled "Polymer Precursor Dispersion Containing a Micropulp and Method of Making the Dispersion", Appln. No. 10/428,294, the disclosures of which are hereby incorporated herein by reference. Generally, a process for preparing a slurry of microfibers includes agitation of fibers, such as commercially available fibers in a dispersion.

Agitation can be accomplished, for example, by refining starting material fibers between rotating discs to cut and shear the fibers into smaller pieces. Processed fibers differ from short fibers by having a multitude of fibrils extending from the body of each pulp particle. The fibrils provide minute hair-like anchors for reinforcing composite materials and cause the processed fibers to have a very high surface area.

A particularly useful starting material is aramid pulp, which is well known in the art and can be made by refining aramid fibers to fibrillate the short pieces of aramid fiber material. Such pulps have been reported to have a surface area in the range of 4.2 to 15

meters<sup>2</sup>/gram and a Kajaani weight average length in the range of 0.6 to 1.1 millimeters (mm). Such pulps have high volume average length, compared to the micropulp. For example, Style 1F543 aramid pulp available from E. I. du Pont de Nemours and Company has a Kajaani weight average length in the range of 0.6 to 0.8 mm, and when laser defraction is used to measure this pulp the volume average length is 500 to 600 micrometers (0.5 to 0.6 mm). An alternate method of 5 making aramid pulp directly from a polymerizing solution is disclosed in U.S. Patent No. 5,028,372. Short fiber (sometimes called floc) is made by cutting continuous filament into short lengths without significantly fibrillating the fiber. Short fiber length typically ranges from about 0.25 10 mm to 12 mm. Short fibers suitable for use in the polyesters are the reinforcing fibers disclosed in U.S. Patent No. 5,474,842. Fibrils are non-granular film-like particles having an average maximum length or dimension in the range of 0.2 to 1 mm with a length-to-width aspect 15 ratio in the range of 5:1 to 10:1. The thickness dimension is on the order of a fraction of a micron. Aramid fibrils are well known in the art and can be made in accordance with the processes disclosed in U.S. Patent Nos. 5,209,877, 5,026,456, 3,018,091 and 2,999,788. The 20 processes typically include adding a solution of organic polymer in solvent to another liquid that is a non-solvent for the polymer but is miscible with the solvent, and applying vigorous agitation to cause coagulation of fibrils. The coagulated fibrils are wet milled, separated, and dried to yield clumps of fibrils having a high surface 25 area; the clumps are then opened to yield a particulate fibril product.

Microfibers for use in the polyesters can be organic or inorganic. The organic microfibers can contain any known organic material used for making fibers. Examples of materials of which organic fibers can be made include synthetic polymers such as 30 aliphatic polyamides, polyesters, polyacrylonitriles, polyvinyl alcohols, polyolefins, polyvinyl chlorides, polyvinylidene chlorides,

polyurethanes, polyfluorocarbons, phenolics, polybenzimidazoles, polyphenylenetriazoles, polyphenylene sulfides, polyoxadiazoles, polyimides, aromatic polyamides; and natural fibers, such as cellulose, cotton, silk, and/or wool fibers.

5 Some commercially available organic fibers useful as a starting material for making microfibers include ZYLON® PBO-AS (poly(p-phenylene-2,6-benzobisoxazole)) fiber, ZYLON® PBO-HM (poly(p-phenylene-2,6-benzobisoxazole)) fiber, DYNEEMA® SK60 and SK71 ultra high strength polyethylene fiber, available from Toyobo, Japan; Celanese VECTRAN® HS pulp, EFT 1063-178, available from Engineering Fibers Technology, Shelton, Connecticut; CFF Fibrillated Acrylic Fiber, available from Sterling Fibers, Inc., Pace, Florida; and Tiara Aramid KY-400S Pulp, available from Daicel Chemical Industries, Ltd., 1 Teppo-Cho, Sakai City Japan.

10 15 For some applications, preferred materials for fibers are certain aromatic polyamide polymers, especially poly(p-phenylene terephthalamide) and/or poly(m-phenylene isophthalamide), which are also known as aramid fibers. As used herein, an "aramid" is a polyamide having amide (-CONH-) linkages of which at least 85% are attached directly to two aromatic rings.

15 20 The fibers can contain known additives. In aramid fibers, one or more other polymeric materials can be blended with the aramid. For example, aramid fibers can contain up to about 10 percent, by weight, of other polymeric materials. If desired, copolymers having as much as 10 percent of one or more other diamines substituted for the diamine of the aramid or as much as 10 percent of other diacid chloride substituted for the diacid chloride of the aramid. Such organic fibers are disclosed in U.S. Patent Nos. 3,869,430; 3,869,429; 3,767,756; and 2,999,788. Preferred aromatic polyamide organic fibers are 25 30 available as KEVLAR® fibers; KEVLAR® aramid pulp, style 1F543; 1.5 mm KEVLAR® aramid floc style 6F561; and NOMEX® aramid fibrils

style F25W, all available from E. I. du Pont de Nemours and Company, Wilmington, Delaware.

Examples of inorganic fibers that can be used include fibers made of glass, carbon fibers, carbon nanotubes, silica carbide fibers, mineral fibers made of, for example, wollastonite (CaSiO<sub>3</sub>), and whiskers, which are single crystals of materials such as, for example, silicon carbide, boron, and boron carbide, and are described in Plastics Additives, 3rd, Gachter and Muller, Hanser Publishers, New York, 1990.

10 Preferred liquid media for the slurry include aqueous and non-aqueous solvents; monomers; and polymer precursors. Polymer precursors suitable as liquid media for the slurry are disclosed in concurrently-filed and co-owned patent application entitled "Polymer Precursor Dispersion Containing a Micropulp and Method of Making the Dispersion", Appl. No. 10/428,294, already incorporated herein by reference.

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An exemplary preferred polymer precursor useful as a liquid medium is ethylene glycol.

20 Suitable polyesters in which the microfibers can be dispersed include homopolymer polyesters such as polypropylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, and polycyclohexane terephthalate; and copolymers. Preferred polyesters are polyethylene terephthalate and copolymers of polyethylene terephthalate and comonomers such as dimethyl isophthalate, dimethyl naphthalate, diethylene glycol, propanediol, butanediol, cyclohexane dimethanol, or dimethyl cyclohexanedicarboxylate.

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30 The polyester compositions of the present invention may be blended with other polymeric materials. Examples of blendable polymeric materials include polyethylene, high density polyethylene, low density polyethylene, linear low density polyethylene, ultralow

density polyethylene, polyolefins, poly(ethylene-co-glycidylmethacrylate), poly(ethylene-co-methyl (meth)acrylate-co-glycidyl acrylate), poly(ethylene-co-n-butyl acrylate-co-glycidyl acrylate), poly(ethylene-co-methyl acrylate), poly(ethylene-co-ethyl acrylate), poly(ethylene-co-butyl acrylate), poly(ethylene-co-(meth)acrylic acid), metal salts of poly(ethylene-co-(meth)acrylic acid), poly((meth)acrylates), such as poly(methyl methacrylate), poly(ethyl methacrylate), and the like, poly(ethylene-co-carbon monoxide), poly(vinyl acetate), poly(ethylene-co-vinyl acetate), poly(vinyl alcohol), poly(ethylene-co-vinyl alcohol), polypropylene, polybutylene, polyesters, poly(ethylene terephthalate), poly(1,3-propylene terephthalate), poly(1,4-butylene terephthalate), PETG, poly(ethylene-co-1,4-cyclohexanedimethanol terephthalate), polyetheresters, poly(vinyl chloride), PVDC, poly(vinylidene chloride), polystyrene, syndiotactic polystyrene, poly(4-hydroxystyrene), novalacs, poly(cresols), polyamides, nylon, nylon 6, nylon 46, nylon 66, nylon 612, polycarbonates, poly(bisphenol A carbonate), polysulfides, poly(phenylene sulfide), polyethers, poly(2,6-dimethylphenylene oxide), polysulfones, copolymers of ethylene with alkyl (meth)acrylates, such as the Elvaloy® polymers available from E.I. du Pont and Company of Wilmington, DE, sulfonated aliphatic-aromatic copolymers, such as are sold under the Biomax® tradename by E.I. du Pont and Company of Wilmington, DE, aliphatic-aromatic copolymers, such as are sold under the Eastar Bio® tradename by the Eastman Chemical Company, (Eastar Bio® is chemically believed to be essentially poly(1,4-butylene adipate-co-terephthalate, (55:45, molar)), sold under the Ecoflex® tradename by the BASF Corporation, (Ecoflex® is believed to be essentially poly(1,4-butylene terephthalate-co-adipate, (50:50, molar) and may be chain-extended through the addition of hexamethylenediisocyanate), and sold under the EnPol® tradename by the Ire Chemical Company, aliphatic polyesters, such as

poly(1,4-butylene succinate), (Bionolle® 1001, from Showa High Polymer Company), poly(ethylene succinate), poly(1,4-butylene adipate-co-succinate), (Bionolle® 3001, from the Showa High Polymer Company), and poly(1,4-butylene adipate) as, for example, sold by the Ire Chemical Company under the tradename of EnPol®, sold by the Showa High Polymer Company under the tradename of Bionolle®, sold by the Mitsui Toatsu Company, sold by the Nippon Shokubai Company, sold by the Cheil Synthetics Company, sold by the Eastman Chemical Company, and sold by the Sunkyon Industries Company, 5 poly(amide esters), for example, as sold under the Bak® tradename by the Bayer Company, (these materials are believed to include the constituents of adipic acid, 1,4-butanediol, and 6-aminocaproic acid), polycarbonates, for example such as poly(ethylene carbonate) sold by the PAC Polymers Company, poly(hydroxyalkanoates), such as 10 poly(hydroxybutyrate)s, poly(hydroxyvalerate)s, poly(hydroxybutyrate-co-hydroxyvalerate)s, for example such as sold by the Monsanto Company under the Biopol® tradename, poly(lactide-co-glycolide-co-caprolactone), for example as sold by the Mitsui Chemicals Company under the grade designations of H100J, S100, and T100, 15 poly(caprolactone), for example as sold under the Tone(R) tradename by the Union Carbide Company and as sold by the Daicel Chemical Company and the Solvay Company, and poly(lactide), for example as sold by the Cargill Dow Company under the tradename of EcoPLA® and the Dianippon Company and the like and copolymers thereof and 20 mixtures thereof.

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In some preferred embodiments of the invention, the polyesters of the invention are blended with one or more tougheners. Tougheners include any material that enhances the durability of a polymer or increases its resistance to impact. Examples of tougheners 30 suitable for use in the present invention include high density polyethylene; glycidyl-functional polymers, such as poly(ethylene-co-

glycidylmethacrylate), poly(ethylene-co-methyl (meth)acrylate-co-glycidyl acrylate), poly(ethylene-co-n-butyl acrylate-co-glycidyl acrylate); poly((meth)acrylates), such as poly(methyl methacrylate), poly(ethyl methacrylate), and the like; polystyrene, syndiotactic polystyrene, poly(4-hydroxystyrene), and the like; novalacs; poly(cresols); polyamides; nylon, including nylon 6, nylon 46, nylon 66, nylon 612, and the like; copolymers of ethylene with alkyl (meth)acrylates, such as the Elvaloy® polymers available from E.I. du Pont and Company of Wilmington, DE; polycarbonates, such as poly(bisphenol A carbonate); polysulfides, and poly(phenylene sulfide).

5 In addition, the polyester compositions produced by the process of the present invention may include one or more fillers. Fillers may tend to increase the Young's modulus, improve the dead-fold properties, improve the rigidity of the film, coating, laminate, or 10 molded article, decrease the cost, and reduce the tendency of the film, coating, or laminate to block or self-adhere during processing or use. The use of fillers has also been found to produce plastic articles which have many of the qualities of paper, such as texture and feel, as 15 disclosed by, for example, Miyazaki, et. al., in US 4,578,296.

20 Fillers suitable for use in the present invention include inorganic, organic and clay fillers, for example, wood flour, gypsum, talc, mica, carbon black, wollastonite, montmorillonite minerals, chalk, diatomaceous earth, sand, gravel, crushed rock, bauxite, limestone, sandstone, aerogels, xerogels, microspheres, porous ceramic spheres, 25 gypsum dihydrate, calcium aluminate, magnesium carbonate, ceramic materials, pozzolanic materials, zirconium compounds, xonotlite, (a crystalline calcium silicate gel), perlite, vermiculite, hydrated or unhydrated hydraulic cement particles, pumice, perlite, zeolites, kaolin, clay fillers, including both natural and synthetic clays and treated and 30 untreated clays, such as organoclays and clays which have been surface treated with silanes and stearic acid to enhance adhesion with

the polyester matrix, smectite clays, magnesium aluminum silicate, bentonite clays, hectorite clays, silicon oxide, calcium terephthalate, aluminum oxide, titanium dioxide, iron oxides, calcium phosphate, barium sulfate, sodium carbonate, magnesium sulfate, aluminum sulfate, magnesium carbonate, barium carbonate, calcium oxide, magnesium oxide, aluminum hydroxide, calcium sulfate, barium sulfate, lithium fluoride, polymer particles, powdered metals, pulp powder, cellulose, starch, chemically modified starch, thermoplastic starch, lignin powder, wheat, chitin, chitosan, keratin, gluten, nut shell flour, wood flour, corn cob flour, calcium carbonate, calcium hydroxide, glass beads, hollow glass beads, seagel, cork, seeds, gelatins, wood flour, saw dust, agar-based materials, reinforcing agents, such as glass fiber, natural fibers, such as sisal, hemp, cotton, wool, wood, flax, abaca, sisal, ramie, bagasse, and cellulose fibers, carbon fibers, graphite fibers, silica fibers, ceramic fibers, metal fibers, stainless steel fibers, recycled paper fibers, for example, from repulping operations, and the like. Titanium dioxide is a preferred filler; however, essentially any filler material known in the art may find use in the polyester compositions of the present invention.

The processes of the invention include providing a slurry containing the microfibers, contacting the slurry with one or more polymerizable components such as, for example, monomers. One process includes ester exchange of dimethyl terephthalate or other suitable ester precursor and ethylene glycol or other suitable glycol, preferably in the presence of an exchange catalyst. Exemplary exchange catalysts include manganese acetate tetrahydrate, zinc acetate dihydrate, and the like. For example, the slurry can be contacted with dimethyl terephthalate and ethylene glycol and formed into polymer by ester exchange followed by polycondensation. As a further example, the slurry may be contacted with the product of an ester exchange reaction, such as bis(2-hydroxyethyl)terephthalate, and then incorporated into a polymer by

polycondensation of monomers at appropriately high temperatures and low pressures, and polymerizing the monomers.

Another exemplary process for preparing a polyester composition containing microfibers includes polyesterification followed by 5 polycondensation. Such processes are preferably carried out in the presence of polycondensation catalysts, such as antimony or titania-based polycondensation catalysts. For example, the slurry containing the microfibers can be introduced into a polyester after an ester exchange reaction and before polycondensation. Preferably, the concentration of 10 microfibers in the slurry for use in such processes is from about 0.01 to about 2.5 weight percent microfibers in the slurry, more preferably from about 0.2 to about 1.0 weight percent. Also preferably, the amount of microfibers in the resulting polymer is preferably from about 0.05 to about 10 weight percent, more preferably from about 0.1 to about 2.5 weight 15 percent, based on the weight of the polymer and microfibers.

The processes of the invention may also include the step of blending the polyester composition with one or more blendable polymeric materials. One or more of the blendable polymeric materials may also function as a toughener.

20 The polymeric material to be blended with the polymer of the present invention may be added to the polyester composition of the present invention at any stage during the polymerization or after the polymerization is completed. For example, the polymeric material may be added with the polyester monomers at the start of the 25 polymerization process. Alternatively, the polymeric material may be added at an intermediate stage of the polymerization, for example, as the precondensate passes into the polymerization vessel. As yet a further alternative, the polymeric material may be added after the polyester exits the polymerizer. For example, the polyester and the 30 polymeric material may be melt fed to any intensive mixing operation,

such as a static mixer or a single- or twin-screw extruder and compounded with the polymeric material.

As yet a further method to produce blends of the polyesters and the polymeric material, the polyester may be combined with the polymeric material in a subsequent post polymerization process.

5                   Typically, such a process would involve intensive mixing of the molten polyester with the polymeric material. Said intensive mixing may be provided through static mixers, Brabender mixers, single screw extruders, twin screw extruders and the like. In a typical process, the 10 polyester would be dried. The polymeric material may also be dried. The dried polyester may then be mixed with the polymeric material.

10                  Alternatively, the polyester and the polymeric material may be cofed through two different feeders. In an extrusion process, the polyester and the polymeric material would typically be fed into the 15 back, feed section of the extruder. However, this should not be considered limiting. The polyester and the polymeric material may be advantageously fed into two different locations of the extruder. For example, the polyester may be added in the back, feed section of the extruder while the polymeric material is fed (or "side-stuffed") into the 20 front of the extruder near the die plate. The extruder temperature profile is set up to allow the polyester to melt under the processing conditions. The screw design will also provide stress and, in turn, heat, to the resin as it mixes the molten polyester with the polymeric material.

25                  Alternatively, the polymeric material may be blended with the polyester material during the formation of the films and coatings of the present invention, as described below.

30                  The processes of the invention may also include the step of adding one or more fillers to the polyester composition. The filler may be added to the polymer of the present invention at any stage during

the polymerization of the polymer or after the polymerization is completed.

For example, the filler may be added with the polyester monomers at the start of the polymerization process. This is preferable for, for example, the silica and titanium dioxide fillers, to provide adequate dispersion of the fillers within the polyester matrix.

5 Alternatively, the filler may be added at an intermediate stage of the polymerization, for example, as the precondensate passes into the polymerization vessel. As yet a further alternative, the filler may be added after the polyester exits the polymerizer. For example, the polyester compositions produced by the processes of the present invention may be melt fed to any intensive mixing operation, such as a static mixer or a single- or twin-screw extruder, and compounded with the filler.

10 15 As yet a further method to produce the filled polyester compositions of the present invention, the polyester composition may be combined with the filler in a subsequent post polymerization process. Typically, such a process would involve intensive mixing of the molten polyester with the filler. Said intensive mixing may be provided through static mixers, Brabender mixers, single screw extruders, twin screw extruders and the like. In a typical process, the polyester would be dried. The dried polyester may then be mixed with the filler. Alternatively, the polyester and the filler may be cofed through two different feeders. In an extrusion process, the polyester and the filler would typically be fed into the back, feed section of the extruder. However, this should not be considered limiting.

20 25 30 The polyester and the filler may also advantageously be fed into two different locations of the extruder. For example, the polyester may be added in the back, feed section of the extruder while the filler is fed (or "side-stuffed") in the front of the extruder near the die plate. The extruder temperature profile is set up to allow the polyester to melt

under the processing conditions. The screw design will also provide stress and, in turn, heat, to the resin as it mixes the molten polyester with the filler. Such processes to melt mix in fillers is disclosed, for example, by Dohrer, et. al., in US 6,359,050.

5           Alternatively, the filler may be blended with the polyester materials during the formation of the films and coatings of the present invention, as described below.

10           Polyesters containing microfibers, as disclosed herein, can be used in making a variety of finished articles. Generally, the polyesters containing microfibers can be used to make any finished article for which polyesters are useful. It has been found that articles made from the polyesters have a desirable balance of physical properties and abrasion resistance for a wide variety of end uses.

15           The polyesters can be used to make monofilaments by known processes such as melt spinning. Monofilaments of the polyesters are useful in making fabrics for use, for example, in making industrial belts.

20           The polyesters are also useful in making molded parts. Molded parts can be made using any known processes used in making molded parts from polyesters.

25           The polyesters are also useful in making films. Films that can be made from the polyesters include cast films, blown films, and oriented films. Films made from the polyesters containing microfibers have been found to have unique surface characteristics. In particular, the presence of the microfibers increases the roughness of the surface of the film, which may be desirable for some applications. An exemplary film preparation process is as follows. A 2 mil cast film was produced on a 1-1/2" Davis portable extruder with a 14" flat sheet die and a chilled casting drum. The 1-1/2" Davis is a 24/1 L/D extruder has four barrel zones which are automatically cooled in case of temperature override. Cooling is done by a closed loop water system.

A barrier screw with a mixing tip was used. 2 mil film was produced using a die gap of 5 mils. The resin was dried for >12 hours @ 225F, in a desiccated oven, prior to extrusion.

Processing conditions:

5	RPM	Feed Zones	Barrel and die zones	head pressure	Chillroll temp	melt temp	takeoff
10	77	480F	500F	610 psi	90 F	527 F	169 in/min

## EXAMPLES

### Example 1

A slurry of fibers was prepared as follows. To a tank charged with 245 lbs of ethylene glycol, 2% or 5 lbs of dry Kevlar® 1F543 pulp was added (250 lbs total batch size). The batch was recirculated through a ball mill at approximately 8 lbs/ min for a total of 16 hrs.

A nominal 4000 lb vertical autoclave with an agitator, vacuum jets and a monomer distillation still located above the clave portion of the autoclave was used to prepare batches of polyester containing microfibers of milled Kevlar® pulp. The monomer still was charged with 1800 liters (approximately 4500 lbs) of dimethyl terephthalate (DMT) and 1050 liters (approximately 2600 lbs) of ethylene glycol. A manganese acetate was used as the ester exchange catalyst and was added as a solution in ethylene glycol. Antimony trioxide was used as the polycondensation polymerization catalyst and was added as a solution in ethylene glycol. In addition, 250 lb of slurry containing 2 % Kevlar® nanopulp in ethylene glycol was added. The temperature of the still was raised to 253 °C over a period of about 170 minutes. Atmospheric pressure was maintained in the still during the ester exchange reaction. An estimated 1500 lbs (approximately 850 liter) of methanol distillate was

recovered. The molten monomer, bis (2-hydroxyethyl) terephthalate, was then dropped from the monomer still to the clave portion of the autoclave.

The ingredients were mixed, agitated, and polymerized by increasing the temperature to 296.6 °C final polymerization temperature.

5 The pressure was reduced to a final pressure of about 0.9 mm Hg over about 165 minutes total polymerization time. The polymer was extruded through casting plate containing approximately 33 holes into strands, which were quenched, cut and boxed.

10 The polymer was tested and found to have an intrinsic viscosity of approximately 0.62 using a solution method. The polymer was also found to have a crystallization temperature of about 129 °C and a melt point of about 257 °C using DSC.

### **Example 2**

15 The polymer from example 1 was molded into dog bone tensile test samples. The item was tested on an Instron tensile tester at 23 °C and 50 % RH. A Crystar® 5005 PET high viscosity control polymer (linear PET homopolymer having an I.V. of 0.85) was molded and tested under the same conditions.

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	<b>Test Polymer (Ex. 1)</b>	<b>Crystar® 5005</b>
25	Max Tensile Stress, ksi	6.4
	Tensile Modulus, ksi	435.5
	% Strain	1.57

### **Example 3**

30 The polymer from example 1 was molded into rectangular samples for testing of flexural properties. The samples were tested on an Instron tensile test machine at 23°C and 50% RH. A commercially available Crystar® PET resin was molded and tested at the same conditions for comparison.

	<b>Test Polymer (Ex 1)</b>	<b>Crystar® 5005</b>
5	<b>Flexural Strength, ksi</b>	14.2
	<b>Flexural Modulus, ksi</b>	462.0
	<b>Max Deflection, inches</b>	0.192
		11.9
		478.7
		0.144

**Example 4**

10                   The polymer from example 1 was molded into rectangular samples for testing of impact properties. The samples were tested on an Izod Impact test machine at 23 °C and 50% RH. A commercially available Crystar® PET resin was molded and tested at the same conditions for comparison. The average Izod impact strength was  
 15                   0.239 ft-lb/in for the polymer from example 1 compared to 0.238 ft-lb/in for the commercially available Crystar 5005 polymer.

**Example 5**

20                   The polymer from example 1 was molded into 4 in disks to determine abrasion by a Taber Abrasion weight loss method. A commercially available Crystar® 5005 was molded and tested at the same conditions. The test used a CS-17 abrasion wheel with an applied load of 1000 grams. The wear index is determined by the weight loss in milligrams per thousand cycles of abrasion, and a  
 25                   smaller wear index is the preferred result. The results showed the wear index for the polymer of example 1 to be an average of 11.75 versus a wear index of 14.68 for the commercial control polymer.

**Example 6**

30                   The polymer from example 1 was melt spun and drawn into a monofilament yarn for evaluation of processing and monofilament properties. The processing conditions and monofilament properties are compared to a commercially available Crystar® 5027 linear PE homopolymer with a 0.72 IV. Polymers were dried overnight at 120 °C

and spun through an 60-80-60 mesh pack screen at the conditions shown below to form a round extrudate.

	Material	Melt Temp °C	Quench Temp °C	Screw Torque Variation, Mg	Screw Speed Variation, rmp	Die Press psi
5	<b>Crystar® 5005</b>	275	140	1600+/- 50	21 +/- 1	370
10	<b>Example 1 Polymer</b>	275	140	3000+/- 1000	30 +/- 10	270

15 The difference in die pressure is thought to be due to the difference in polymer inherent viscosity. The test polymer from Example 1 did not result in any pack pressure build up over the extrusion time for the item.

20 The monofilaments were mechanically drawn in multiple stage with heat applied at constant tension between draw modules. Monofilament properties for the polymer of example 1 are shown below and compared to the properties for a commercial Crystar® 5027 PET resin.

	Material	Draw Ratio	Tenacity, gpd	Elongation, %	Shrinkage, @204 °C
25	<b>Example 1 Polymer</b>	~ 3.5	~ 2.8	~70	~ 3
30	<b>Example 1 Polymer</b>	~ 4.15	~ 3.0	~50	~ 6
35	<b>Example 1 Polymer</b>	~ 4.55	~ 3.7	~25	~15
	<b>Crystar® 5027</b>	~4.55	~3.8	~20	-

40 The abrasion resistance was evaluated for monofilaments produced from the Example 1 polymer as well as for the control Crystar® 5027 polymer. The abrasion resistance was determined using a wire squirrel cage test machine. The monofilaments are

loaded to 850 grams and then placed in contact with a set of rotating wires. In this method the abrasion resistance is measured as the cycles (of the rotating wires) before monofilament failure, such that a higher number means better abrasion resistance. The polymer of example 1 showed an abrasion resistance approximately equal to that of the Crystar® 5027 control.

5 **Example 7**

Polymer from Example 1 was solid phase polymerized. The 10 polymer produced in Example 1 was evaluated and found to have an IV of approximately 0.7 by the Instron method. Approximately 300 lbs of polymer made in Example 1 was put into a horizontal tumble reactor. The temperature was increased from 25 °C to 135 °C over 220 minutes and the flake was held at 135 °C for 180 minutes to effect 15 crystallization. The temperature was then raised to 235 °C over 150 minutes. The material was held at temperature for 90 minutes, cooled, and packed out. The final polymer IV was found to be approximately 0.75 by the Instron method which has been determined to be equivalent to 0.72 IV by the solution method.

20

**Example 8**

Polymer from Example 1 was solid phase polymerized. The 25 polymer produced in example 1 was evaluated and found to have an IV of approximately 0.7 by the Instron method. Approximately 300 lbs of polymer made in example 1 was put into a horizontal tumble reactor. The temperature was increased from 25°C to 135°C over 220 minutes and the flake was held at 135°C for 180 minutes to effect crystallization. The temperature was then raised to 234°C over 30 approximately 160 minutes. The material was held at temperature for approximately 500 minutes, cooled, and packed out. The final polymer IV was found to be approximately 0.88 by the Instron method which

has been determined to be equivalent to 0.92 IV by the solution method versus a target of 0.95 IV solution equivalent.

### Example 9

5                   The polymer from example 7 was melt spun and drawn into a monofilament yarn for evaluation of processing and monofilament properties. The processing conditions and monofilament properties are compared to a commercially available Crystar® 5027 PET with a 0.72 IV. Polymers were dried overnight at 120°C and spun through a  
10                  60-80-60 mesh pack screen at the conditions shown below to form a round extrudate.

	Material	Melt Temp °C	Quench Temp °C	Screw Torque Variation, Mg	Screw Speed Variation, rmp	Die Press psi
15	<b>Crystar® 5027 PET</b>	275	140	1600+/- 50	21 +/- 1	370
20	<b>Example 7 Polymer</b>	273	140	2600+/- 100	22	500

25                  The monofilaments were mechanically drawn in multiple stage with heat applied at constant tension between draw modules. Monofilament properties for the polymer of example 7 are shown below and compared to the properties for a commercial Crystar® 5027 PET resin.

	Material	Draw Ratio	Ten gpd	Modulus gpd	Elong, %	Shrinkage @ 204 C
30	<b>Example 7 Polymer</b>	4.56	3.7	94	23	22
35	<b>Crystar® 5027</b>	4.56	3.5	95	33	22

The abrasion resistance was evaluated for monofilaments produced from the example 7 polymer as well as for the control

Crystar® 5027 polymer. The abrasion resistance was determined using a wire squirrel cage test machine. The monofilaments are loaded to 850 grams and then placed in contact with a set of rotating wires. In this method the abrasion resistance is measured as the cycles (of the rotating wires) before monofilament failure, such that a higher number means better abrasion resistance. The polymer of example 7 showed an abrasion resistance of approximately 7400 +/- 300 cycles versus an average of 4000 +/- 500 cycles to failure for the Crystar® 5027 control.

10

#### Example 10

The polymer from example 8 was melt spun and drawn into a monofilament yarn for evaluation of processing and monofilament properties. The processing conditions and monofilament properties are compared to a commercially available Crystar® 5129 linear PET homopolymer with a 0.95 IV. Polymers were dried overnight at 120° C and spun through an 60-80-60 mesh pack screen at the conditions shown below to form a round extrudate.

	Material	Melt Temp °C	Quench Temp °C	Screw Torque Variation, Mg	Screw Speed Variation, rmp	Die Press psi
20	<b>Crystar® 5129 PET</b>	273	140	2800 +/- 100	15	890
25	<b>Example 8 Polymer</b>	273	140	4000 +/- 100	15	910

The monofilaments were mechanically drawn in multiple stage with heat applied at constant tension between draw modules. Monofilament properties for the polymer of example 8 are shown below and compared to the properties for a commercial Crystar® 5027 PET resin.

Material	Draw Ratio	Ten gpd	Modulus gpd	Elong, %	Shrinkage @ 204 C
5 Example 8 Polymer	4.56	4.1	92	20	26
Crystar® 5129	4.56	4.1	90	19	25

10 The abrasion resistance was evaluated for monofilaments produced from the example 8 polymer as well as for the control Crystar® 5129 polymer. The abrasion resistance was determined using a wire squirrel cage test machine. The monofilaments are loaded to 500 grams and then placed in contact with a set of rotating wires. In this method the abrasion resistance is measured as the cycles (of the rotating wires) before monofilament failure, such that a higher number means better abrasion resistance. The polymer of example 8 showed an abrasion resistance of approximately 15400 +/- 3300 cycles versus an average of 10700 +/- 1050 cycles to failure for the Crystar® 5129 control.

### Example 11: Synthesis of PET with 0.5 wt % Kevlar® microfibers

To a 250 milliliter glass flask was added bis(2-hydroxyethyl)terephthalate, (134.75 grams), manganese(II) acetate tetrahydrate, (0.0468 grams), antimony(III) oxide, (0.0367 grams), and slurry (2 weight percent Kevlar® pulp in ethylene glycol, 25.70 grams slurry). The reaction mixture was stirred and heated to 180 °C under a slow nitrogen purge. After achieving 180 °C, the reaction mixture was stirred at 180 °C for 0.2 hours under a slow nitrogen purge. The reaction mixture was then heated to 285 °C over 0.6 hours with stirring. After achieving 285 °C, the reaction mixture was stirred at 285 °C for 0.7 hours under a slow nitrogen purge. 41.6 grams of a colorless distillate was collected over this heating cycle. The reaction mixture was then staged to full vacuum with stirring at 285 °C. The resulting

reaction mixture was stirred for 0.9 hours under full vacuum, (pressure less than 100 mtorr). The vacuum was then released with nitrogen and the reaction mass allowed to cool to room temperature. An additional 16.7 grams of distillate was recovered and 92.6 grams of a solid product was recovered.

A sample of the product was measured for laboratory relative viscosity, (LRV), as described above and was found to have an LRV of 19.33. This sample was calculated to have an inherent viscosity of 0.60 dL/g. The sample also underwent differential scanning 10 calorimetry, (DSC), analysis. A glass transition temperature, (Tg), was observed with an onset of 72.2 °C, a midpoint of 78.3 °C, and an endpoint of 84.4 °C. A crystalline melting temperature, (Tm), was observed at 252.5 °C, (47.0 J/g).

15 **Example 12: Synthesis of PET homopolymer with 2.5 wt % Kevlar® microfibers**

To a 500 milliliter glass flask was added bis(2-hydroxyethyl)terephthalate, (134.75 grams), manganese(II) acetate tetrahydrate, (0.0454 grams), antimony(III) oxide, (0.0375 grams), and 20 Kevlar® pulp slurry, (2 weight percent Kevlar® pulp in ethylene glycol, 130.46 grams slurry). The reaction mixture was stirred and heated to 180 °C under a slow nitrogen purge. After achieving 180 °C, the reaction mixture was stirred at 180 °C for 0.2 hours under a slow nitrogen purge. The reaction mixture was then heated to 285 °C over 25 0.9 hours with stirring. After achieving 285 °C, the reaction mixture was stirred at 285 °C for 0.8 hours under a slow nitrogen purge. 132.1 grams of a colorless distillate was collected over this heating cycle. The reaction mixture was then staged to full vacuum with stirring at 285 °C. The resulting reaction mixture was stirred for 1.0 hour under full 30 vacuum, (pressure less than 100 mtorr). The vacuum was then released with nitrogen and the reaction mass allowed to cool to room

temperature. An additional 27.5 grams of distillate was recovered and 92.5 grams of a solid product was recovered.

A sample of the product was measured for laboratory relative viscosity, (LRV), as described above and was found to have an LRV of 5 19.38. This sample was calculated to have an inherent viscosity of 0.60 dL/g. The sample also underwent differential scanning 10 calorimetry, (DSC), analysis. A glass transition temperature, (Tg), was observed with an onset of 72.2 °C, a midpoint of 77.5 °C, and an endpoint of 83.1°C. A crystalline melting temperature, (Tm), was observed at 256.6 °C, (44.9 J/g).

**Example 13: Sodiosulfoisophthalate copolyester with 0.25 wt % Kevlar® microfibers**

To a 500 milliliter glass flask was added bis(2-15 hydroxyethyl)terephthalate, (298.99 grams), dimethyl 5-sulfoisophthalate, sodium salt, (7.11 grams), sodium acetate, (0.33 grams), manganese(II) acetate tetrahydrate, (0.1039 grams), antimony(III) oxide, (0.0836 grams), and Kevlar® pulp slurry, (2 weight percent Kevlar® pulp in ethylene glycol, 61.20 grams slurry). The 20 reaction mixture was stirred and heated to 180 °C under a slow nitrogen purge. After achieving 180 °C, the reaction mixture was stirred at 180 °C for 0.5 hours under a slow nitrogen purge. The reaction mixture was then heated to 285 °C over 1.9 hours with stirring. After achieving 285 °C, the reaction mixture was stirred at 285 °C for 25 0.7 hours under a slow nitrogen purge. 103.4 grams of a colorless distillate was collected over this heating cycle. The reaction mixture was then staged to full vacuum with stirring at 285 °C. The resulting reaction mixture was stirred for 0.8 hours under full vacuum, (pressure less than 100 mtorr). The vacuum was then released with nitrogen and 30 the reaction mass allowed to cool to room temperature. An additional

23.0 grams of distillate was recovered and 200.0 grams of a solid product was recovered.

A sample of the product was measured for laboratory relative viscosity, (LRV), as described above and was found to have an LRV of 14.70. This sample was calculated to have an inherent viscosity of 0.51 dL/g. The sample underwent differential scanning calorimetry, (DSC), analysis. A glass transition temperature, (T<sub>g</sub>), was observed with an onset of 79.9 °C, a midpoint of 80.4 °C, and an endpoint of 80.8 °C. A crystalline melting temperature, (T<sub>m</sub>), was observed at 247.0 °C, (46.6 J/g).

**Example 14: Isophthalate copolyester with 0.5 wt % Kevlar® microfibers**

To a 500 milliliter glass flask was added bis(2-hydroxyethyl)terephthalate, (183.05 grams), isophthalic acid, (79.74 grams), manganese(II) acetate tetrahydrate, (0.1039 grams), antimony(III) oxide, (0.0836 grams), and Kevlar® pulp slurry, (2 weight percent Kevlar® pulp in ethylene glycol, 60.6 grams slurry). The reaction mixture was stirred and heated to 180 °C under a slow nitrogen purge. After achieving 180°C, the reaction mixture was stirred at 180 °C for 0.4 hours under a slow nitrogen purge. The reaction mixture was then heated to 285 °C over 2.2 hours with stirring. After achieving 285 °C, the reaction mixture was stirred at 285 °C for 0.7 hours under a slow nitrogen purge. 62.1 grams of a colorless distillate was collected over this heating cycle. The reaction mixture was then staged to full vacuum with stirring at 285 °C. The resulting reaction mixture was stirred for 1.6 hours under full vacuum, (pressure less than 100 mtorr). The vacuum was then released with nitrogen and the reaction mass allowed to cool to room temperature. An additional 26.6 grams of distillate was recovered and 216.7 grams of a solid product was recovered.

A sample of the product was measured for laboratory relative viscosity, (LRV), as described above and was found to have an LRV of 23.68. This sample was calculated to have an inherent viscosity of 0.67 dL/g. The sample underwent differential scanning calorimetry, (DSC), analysis. A glass transition temperature, (Tg), was observed with an onset of 67.8 °C, a midpoint of 69.7°C, and an endpoint of 71.6°C.

**Example 15: Synthesis of 3GT with 0.5 wt % Kevlar® microfibers**

10 To a 250 milliliter glass flask was added dimethyl terephthalate, (95.15 grams), 1,3-propanediol, (59.66 grams), Tyzor® PEL-G, (8.2 weight percent titanium, 0.1212 grams), and Kevlar® pulp slurry, (2 weight percent Kevlar® pulp in ethylene glycol, 25.36 grams slurry). The reaction mixture was stirred and heated to 180 °C under a slow nitrogen purge. After achieving 180 °C, the reaction mixture was stirred at 180 °C for 0.6 hours under a slow nitrogen purge. The reaction mixture was then heated to 190 °C over 0.1 hours with stirring. After achieving 190 °C, the reaction mixture was stirred at 190 °C for 0.6 hours under a slight nitrogen purge. The reaction mixture was then heated to 200 °C over 0.2 hours with stirring. After achieving 200 °C, the reaction mixture was stirred at 200 °C for 0.7 hours under a slight nitrogen purge. The reaction mixture was then heated to 255 °C over 0.8 hours with stirring. After achieving 255 °C, the reaction mixture was stirred at 255 °C for 0.6 hours under a slow nitrogen purge. 48.6 grams of a colorless distillate was collected over this heating cycle.

15 The reaction mixture was then staged to full vacuum with stirring at 255 °C. The resulting reaction mixture was stirred for 1.4 hours under full vacuum, (pressure less than 100 mtorr). The vacuum was then released with nitrogen and the reaction mass allowed to cool to room temperature. An additional 18.5 grams of distillate was recovered and 90.1 grams of a solid product was recovered.

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A sample of the product was measured for laboratory relative viscosity, (LRV), as described above and was found to have an LRV of 28.62. This sample was calculated to have an inherent viscosity of 0.76 dL/g. The sample underwent differential scanning calorimetry, (DSC), analysis. A glass transition temperature, (Tg), was observed with an onset of 47.2 °C, a midpoint of 55.3 °C, and an endpoint of 63.2 °C. A crystalline melting temperature, (Tm), was observed at 218.0 °C, (41.0 J/g).

10 **Example 16: Synthesis of 4GT with 1 wt % Kevlar® microfibers**

To a 250 milliliter glass flask was added dimethyl terephthalate, (89.33 grams), 1,4-butanediol, (66.69 grams), Tyzor® PEL-G, (8.2 weight percent titanium, 0.1282 grams), and Kevlar® pulp slurry, (2 weight percent Kevlar® pulp in ethylene glycol, 51.11 grams slurry). The reaction mixture was stirred and heated to 180 °C under a slow nitrogen purge. After achieving 180 °C, the reaction mixture was stirred at 180 °C for 0.3 hours under a slow nitrogen purge. The reaction mixture was then heated to 190 °C over 0.1 hours with stirring. After achieving 190 °C, the reaction mixture was stirred at 190 °C for 0.5 hours under a slight nitrogen purge. The reaction mixture was then heated to 200 °C over 0.1 hours with stirring. After achieving 200 °C, the reaction mixture was stirred at 200 °C for 0.5 hours under a slight nitrogen purge. The reaction mixture was then heated to 255 °C over 0.3 hours with stirring. After achieving 255 °C, the reaction mixture was stirred at 255 °C for 0.8 hours under a slow nitrogen purge. 73.1 grams of a colorless distillate was collected over this heating cycle. The reaction mixture was then staged to full vacuum with stirring at 255 °C. The resulting reaction mixture was stirred for 0.6 hours under full vacuum, (pressure less than 100 mtorr). The vacuum was then released with nitrogen and the reaction mass allowed to cool to room

temperature. An additional 21.5 grams of distillate was recovered and 92.0 grams of a solid product was recovered.

A sample of the product was measured for laboratory relative viscosity, (LRV), as described above and was found to have an LRV of 5 30.17. This sample was calculated to have an inherent viscosity of 0.79 dL/g. The sample underwent differential scanning calorimetry, (DSC), analysis. A glass transition temperature, (Tg), was observed with an onset of 40.1 °C, a midpoint of 46.4 °C, and an endpoint of 52.7 °C. A crystalline melting temperature, (Tm), was observed at 201.8 °C, 10 (45.8 J/g).

#### Results for Examples 11 through 16

	Example	Polymer Composition	Kevlar(R) (wt. %)	Finishing Time (hr)	Calc IV (dL/g)	Tm (°C, (J/g))
15	11	2G/T	0.5	0.9	0.60	252.5(47.0)
20	12	2G/T	2.5	1.0	0.60	256.6(44.9)
	13	2G/T:DRL-6 (98:2)	0.25	0.8	0.51	247.0 (46.6)
25	14	2G/T:I (60:40)	0.5	1.6	0.67	[note: Tg = 69.7]
	15	2G:3G/T	0.5	1.4	0.76	218.0 (41.0)
	16	2G:4G/T	1.0	0.6	0.79	201.8 (45.8)